

TITLE

Star Polymer Lubricating Composition

FIELD OF INVENTION

The present invention relates to a lubricating composition containing a polymer such as a star polymer, an antiwear agent and a corrosion inhibitor. The invention further provides a method for lubricating a mechanical device using the lubricating composition.

BACKGROUND OF THE INVENTION

[0001] The use of star polymers in lubricating compositions is known. The star polymers known in lubricating compositions are summarised in the prior art below.

[0002] International Application WO 04/087850 discloses lubricating compositions containing block copolymers prepared from RAFT (Reversible Addition Fragmentation Transfer) or ATRP (Atom Transfer Radical Polymerisation) polymerisation processes. The polymers have frictional properties. The block copolymer may have di-block, tri-block, multi-block, comb and/or star architecture. However, no guidance is given on methods suitable to prepare star copolymers. Also disclosed are polymers suitable for greases, motor oils, gearbox oils, turbine oils, hydraulic fluids, pump oils, heat transfer oils, insulation oils, cutting oils and cylinder oils.

[0003] US Patent Application US05/038146 discloses star polymers derived from (i) a core portion comprising a polyvalent (meth) acrylic monomer, oligomer or polymer thereof or a polyvalent divinyl non-acrylic monomer, oligomer or polymer thereof; and (ii) at least two arms of polymerized alkyl (meth)acrylate ester. The polymers may be prepared by RAFT, ATRP or nitroxide mediated techniques.

[0004] International Application WO 96/23012 discloses star-branched polymers prepared from acrylic or methacrylic monomers. The polymers have a core or nucleus derived from acrylate or methacrylate esters of polyols. Further the polymers have molecular weights and other physical characteristics

that make them useful for lubricating oil compositions. The star-branched polymers disclosed are prepared by anionic polymerisation techniques.

[0005] The star polymers of EP 979 834 require from 5 to 10 weight percent of a C16 to C30 alkyl (meth)acrylate and from 5 to 15 weight percent of butyl methacrylate. A viscosity index improver with a C16 to C30 alkyl (meth)acrylate monomer present at 5 weight percent or more has reduced low temperature viscosity performance because the polymer has a waxy texture.

[0006] US Patent 5,070,131 disclose gear oil compositions having improved shear stability index essentially consisting of gear oil, a viscosity index improver comprising a hydrogenated star polymer comprising at least four arms, the arms comprising, before hydrogenation, polymerized conjugated diolefin monomer units and the arms having a number average molecular weight within the range of 3,000 to 15,000.

[0007] None of the prior art references above disclose fully formulated lubricating compositions that simultaneously achieve acceptable viscosity index (VI), oil blend thickening capabilities, improved fuel economy, shear stability, good low temperature viscosity performance, and low viscosity modifier treatment level whilst maintaining the appropriate lubricating performance for a mechanical device, such as hydraulic systems.

[0008] In view of the prior art it would be advantageous to have a lubricating composition containing a polymer that is capable of providing acceptable viscosity index (VI), oil blend thickening capabilities, shear stability, good low temperature viscosity performance, and low viscosity modifier treatment level whilst maintaining the appropriate lubricating performance for a mechanical device.

[0009] The present invention provides a lubricating composition capable of providing acceptable viscosity index (VI), oil blend thickening capabilities, shear stability, good low temperature viscosity performance, and low viscosity modifier treatment level whilst maintaining the appropriate lubricating performance for a mechanical device.

[0010] The prior art references, specifically WO 96/23012 and US 5,070,131 employ anionic polymerisation techniques to prepare the polymer.

Anionic polymerisation techniques are believed to involve complex processes that require systems to be substantially water-free, acid-free, oxygen-free, dry, clean, and have non-contaminated vessels. In one particular embodiment it would be advantageous to have a lubricating composition that does not require a polymer prepared with complex processes that require oxygen-free, dry, clean, non-contaminated vessels. In one embodiment the lubricating composition contains a polymer that does not require preparation by anionic polymerisation techniques.

SUMMARY OF THE INVENTION

[0011] In one embodiment the invention provides a lubricating composition comprising:

(a) about 0.001 to about 15 wt % of a polymer with (i) a weight average molecular weight of about 120,000 to about 700,000; and (ii) a shear stability index of about 30 to about 60;

(b) an antiwear agent;

(c) a corrosion inhibitor; and

(d) an oil of lubricating viscosity.

[0012] In one embodiment the invention provides a lubricating composition comprising:

(a) about 0.001 to about 15 wt % of a polymer with (i) a weight average molecular weight of about 120,000 to about 700,000; and (ii) a shear stability index of about 30 to about 60;

(b) an antiwear agent;

(c) a corrosion inhibitor;

(d) a detergent; and

(e) an oil of lubricating viscosity.

[0013] In one embodiment the invention provides a lubricating composition comprising:

(a) about 0.001 to about 15 wt % of a polymer with (i) a weight average molecular weight of about 120,000 to about 700,000; and (ii) a shear stability index of about 30 to about 60;

(b) about 0.0001 wt % to about 5 wt % of an antiwear agent;

- (c) 0.0001 wt % to about 5 wt % of a corrosion inhibitor;
- (d) about 0 wt % to about 3 wt % of a detergent; and
- (e) about 87 wt % to about 99.98 wt % of an oil of lubricating viscosity.

[0014] In one embodiment the invention provides a lubricating composition comprising:

- (a) about 0.001 to about 15 wt % of a polymer with radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0015] In one embodiment the invention provides a lubricating composition comprising:

- (a) about 0.001 to about 15 wt % of a polymer with radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor;
- (d) a detergent; and
- (e) an oil of lubricating viscosity.

[0016] In one embodiment the invention provides a lubricating composition comprising:

- (a) about 0.001 to about 15 wt % of a polymer with a weight average molecular weight of about 50,000 to about 1,000,000, wherein the polymer has radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0017] In one embodiment the invention provides a lubricating composition comprising:

- (a) about 0.001 to about 15 wt % of a polymer with radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor;

- (d) a detergent; and
- (e) an oil of lubricating viscosity.

[0018] In one embodiment the invention provides a lubricating composition comprising:

- (a) about 0.001 to about 15 wt % of a polymer with a weight average molecular weight of about 50,000 to about 1,000,000, wherein the polymer has radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor;
- (d) a detergent; and
- (e) an oil of lubricating viscosity.

[0019] In one embodiment the invention provides a method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device comprises at least one of an internal combustion engine, a hydraulic system, a turbine system, a circulating oil system, or an industrial oil system a gear, a gearbox or a transmission, and wherein the lubricating composition comprises:

- (a) about 0.001 to about 15 wt % of a polymer with (i) a weight average molecular weight of about 120,000 to about 700,000; and (ii) a shear stability index of about 30 to about 60;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0020] In one embodiment the invention provides a method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device comprises at least one of an internal combustion engine, a hydraulic system, a turbine system, a circulating oil system, or an industrial oil system, a gear, a gearbox or a transmission, and wherein the lubricating composition comprises:

- (a) about 0.001 to about 15 wt % of a polymer with radial or star architecture;
- (b) an antiwear agent;

- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0021] In one embodiment the invention provides a method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device comprises at least one of an internal combustion engine, a hydraulic system, a turbine system, a circulating oil system, or an industrial oil system, a gear, a gearbox or a transmission, and wherein the lubricating composition comprises:

- (a) about 0.001 to about 15 wt % of a polymer with a weight average molecular weight of about 50,000 to about 1,000,000, wherein the polymer has radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0022] In one embodiment the invention provides a method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device is hydraulic system, and wherein the lubricating composition comprises:

- (a) a polymer derived from about 20 wt % or more of a mono-vinyl monomer, wherein the polymer is present at about 0.001 to about 15 wt % of the lubricating composition, wherein the polymer has (i) a weight average molecular weight of about 120,000 to about 700,000; and (ii) a shear stability index of about 30 to about 60;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

[0023] In one embodiment the invention provides a method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device is a hydraulic system, and wherein the lubricating composition comprises:

- (a) about 0.001 to about 15 wt % of a polymer with a weight average molecular weight of about 50,000 to about 1,000,000, wherein the polymer has radial or star architecture;
- (b) an antiwear agent;
- (c) a corrosion inhibitor; and
- (d) an oil of lubricating viscosity.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The present invention provides a lubricating composition and a method for lubricating a mechanical device as disclosed above.

Polymer

[0025] As used herein terms such as “the polymer has (or contains) monomers composed of” means the polymer comprises units derived from the particular monomer referred to.

[0026] In different embodiments the polymer may contain about 20 wt % or more, or greater than 50 wt %, or about 55 wt % or more, or about 70 wt % or more, or about 90 wt % or more, or about 95 wt % or more, or about 100 wt % of a non-diene monomer (that is to say, non-diene monomer units or units derived from polymerisation of one of more non-diene monomers). Examples of diene monomers include 1,3-butadiene or isoprene. Examples of a non-diene or mono-vinyl monomer include styrene, methacrylates, or acrylates.

[0027] In one embodiment the polymer may be derived from about 20 wt % or more of a mono-vinyl monomer, wherein the polymer has a weight average molecular weight of about 50,000 to about 1,000,000, and wherein the polymer has radial or star architecture.

[0028] When the polymer is a radial or star polymer, the amount of mono-vinyl monomer as described above refers only to the composition of the polymeric arms, i.e., the wt % values as given are exclusive of any di-functional (or higher) monomer found in a polymer core.

[0029] As described hereinafter the molecular weight of the viscosity modifier has been determined using known methods, such as GPC analysis using polystyrene standards. Methods for determining molecular weights of polymers are well known. The methods are described for instance: (i) P.J. Flory,

“Principles of Polymer Chemistry”, Cornell University Press 1953), Chapter VII, pp 266-315; or (ii) “Macromolecules, an Introduction to Polymer Science”, F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312. As used herein the weight average and number weight average molecular weights of the polymers of the invention are obtained by integrating the area under the peak corresponding to the polymer of the invention, which is normally the major high molecular weight peak, excluding peaks associated with diluents, impurities, uncoupled polymer chains and other additives. Typically, the polymer of the invention has radial or star architecture.

[0030] The weight average molecular weight of the polymer may be in the range of about 50,000 to about 1,000,000, or about 100,000 to about 800,000, or about 120,000 to about 700,000.

[0031] As used herein the shear stability index (SSI) may be determined by a 20 hour KRL test (Volkswagen Tapered Bearing Roller Test). The test procedure is set out in both CEC-L-45-A-99 and DIN 51350-6-KRL/C. The polymer SSI may be in the range of about 20 to about 90, or about 15 to about 75, or about 30 to about 60.

[0032] In different embodiments the polymer may have a weight average molecular weight of about 50,000 to about 1,000,000 and a SSI of about 10 to about 100, or about 20 to about 90; or the polymer may have a weight average molecular weight of about 100,000 to about 800,000 and a SSI of about 15 to about 75; or the polymer may have a weight average molecular weight of about 120,000 to about 700,000 and a SSI of about 30 to about 60.

[0033] The polymer may be a homopolymer or a copolymer. In one embodiment the polymer is a copolymer. The polymer may have a branched, a comb-like, a radial or a star architecture. In one embodiment the polymer may be a radial or star polymer, or mixtures thereof. The polymer may be a polymer having a random, tapered, di-block, tri-block or multi-block architecture. Typically the polymer has random or tapered architecture.

[0034] When the polymer has branched, comb-like, radial or star architecture, the polymer has polymeric arms. For such materials, the polymeric arms may have block architecture, or hetero architecture, or tapered block architecture. Tapered-arm architecture has a variable composition across

the length of a polymer arm. For example, the tapered arm may be composed of, at one end, a relatively pure first monomer and, at the other end, a relatively pure second monomer. The middle of the arm is more of a gradient composition of the two monomers.

[0035] The polymer derived from a block-arm typically contains one or more polymer arms derived from two or more monomers in block structure within the same arm. A more detailed description of the block-arm is given in Chapter 13 (pp. 333-368) of "Anionic Polymerization, Principles and Practical Applications" by Henry Hsieh and Roderic Quirk (Marcel Dekker, Inc, New York, 1996) (hereinafter referred to as Hsieh et al.).

[0036] The hetero-arm, or "mikto-arm," polymeric arm architecture typically contains arms which may vary from one another either in molecular weight, composition, or both, as defined in Hsieh et al., cited above. For example, a portion of the arms of a given polymer may be of one polymeric type and a portion of a second polymeric type. More complex hetero-arm polymers may be formed by combining portions of three or more polymeric arms with a coupling agent.

[0037] When the polymer has radial or star architecture the polymeric arms may be chemically bonded to a core portion. The core portion may be a polyvalent (meth) acrylic monomer, oligomer, polymer, or copolymer thereof, or a polyvalent divinyl non-acrylic monomer, oligomer polymer, or copolymer thereof. In one embodiment the polyvalent divinyl non-acrylic monomer is divinyl benzene. In one embodiment the polyvalent (meth)acrylic monomer is an acrylate or methacrylate ester of a polyol or a methacrylamide of a polyamine, such as an amide of a polyamine, for instance a methacrylamide or an acrylamide. In different embodiments the polyvalent (meth)acrylic monomer is (i) a condensation reaction product of an acrylic or methacrylic acid with a polyol or (ii) a condensation reaction product of an acrylic or methacrylic acid with a polyamine.

[0038] The polyol which may be condensed with the acrylic or methacrylic acid in different embodiments may contain about 2 to about 20, or about 3 to about 15, or about 4 to about 12 carbon atoms; and the number of hydroxyl

groups present may be about 2 to about 10, or about 2 to about 4, or about 2. Examples of polyols include ethylene glycol, poly (ethylene glycols), alkane diols such as 1,6-hexanene diol or triols such as trimethylolpropane, oligomerised trimethylolpropanes such as Boltorn® materials sold by Perstorp Polyols. Examples of polyamines include polyalkylenepolyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylene pentamine, pentaethylenehexamine and mixtures thereof.

[0039] Examples of the polyvalent unsaturated (meth)acrylic monomer include ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, glycerol diacrylate, glycerol triacrylate, mannitol hexaacrylate, 4-cyclohexanediol diacrylate, 1,4-benzenediol dimethacrylate, pentaerythritol tetraacrylate, 1,3-propanediol diacrylate, 1,5-pentanediol dimethacrylate, bis-acrylates and methacrylates of polyethylene glycols of molecular weight about 200 to about 4000, polycaprolactonediol diacrylate, pentaerythritol triacrylate, 1,1,1-trimethylolpropane triacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,1,1-trimethylolpropane trimethacrylate, hexamethylenediol diacrylate or hexamethylenediol dimethacrylate or an alkylene bis-(meth)acrylamide.

[0040] The amount of polyvalent coupling agent may be an amount suitable to provide coupling of polymer previously prepared as arms onto a core comprising the coupling agent in monomeric, oligomeric, or polymeric form, to provide a star polymer. As described above, suitable amounts may be determined readily by the person skilled in the art with minimal experimentation, even though several variables may be involved. For example, if an excessive amount of coupling agent is employed, or if excessive unreacted monomer from the formation of the polymeric arms remains in the system, crosslinking rather than star formation may occur. Typically the mole ratio of polymer arms to coupling agent may be about 50:1 to about 1.5:1 (or 1:1), or about 30:1 to about 2:1, or about 10:1 to about 3:1, or about 7:1 to about 4:1, or about 4:1 to about 1:1. In other embodiments the mole ratio of polymer arms to coupling agent may be about 50:1 to about 0.5:1, or about

30:1 to about 1:1, or about 7:1 to about 2:1. The desired ratio may also be adjusted to take into account the length of the arms, longer arms sometimes tolerating or requiring more coupling agent than shorter arms. Typically the material prepared is soluble in an oil of lubricating viscosity.

[0041] In one embodiment the polymeric arms of the polymer have a polydispersity of about 2 or less, or about 1.7 or less, or about 1.5 or less, for instance, about 1 to about 1.4 as measured before radial or star polymer formation or on uncoupled units. In one embodiment the overall polymer composition, which includes the polymer with radial or star architecture, has polydispersity with a bimodal or higher modal distribution. The bimodal or higher distribution in the overall polymer composition is believed to be partially due to the presence of varying amounts of uncoupled polymer chains and/or uncoupled radial or star-polymers or star-to-star coupling formed as the polymer is prepared.

[0042] The overall polymer composition with the radial or star architecture may thus also have uncoupled polymeric arms present (also referred to as a polymer chain or linear polymer). The percentage conversion of a polymer chain to radial or star polymer may be at least about 10 %, or at least about 20 %, or at least about 40 %, or at least about 55 %, for instance at least about 70 %, at least about 75 % or at least about 80%. In one embodiment the conversion of polymer chain to radial or star polymer may be about 90 %, or about 95 %, or about 100%. In one embodiment a portion of the polymer chains does not form a star polymer and remains as a linear polymer. In one embodiment the polymer is a mixture of (i) a polymer with radial or star architecture, and (ii) linear polymer chains (also referred to as uncoupled polymeric arms). In different embodiments the amount of radial or star architecture within the polymer composition may be about 10 wt % to about 85 wt %, or about 25 wt % to about 70 wt % of the amount of polymer. In different embodiments the linear polymer chains may be present at about 15 wt % to about 90 wt %, or about 30 wt % to about 75 wt % of the amount of polymer.

[0043] The polymer with branched, comb-like, radial or star architecture may have 2 or more arms, or about 5 or more arms, or about 7 or more arms, or

10 or more arms, for instance about 12 to about 100, or about 14 to about 50, or about 16 to about 40 arms. The polymer with branched, comb-like, radial or star architecture may have about 120 arms or less, or about 80 arms or less, or about 60 arms or less.

[0044] The polymer may be obtained/obtainable from a controlled radical polymerisation technique. Examples of a controlled radical polymerisation technique include RAFT, ATRP or nitroxide mediated processes. The polymer may also be obtained/obtainable from anionic polymerisation processes. In one embodiment the polymer may be obtained/obtainable from RAFT, ATRP or anionic polymerisation processes. In one embodiment the polymer may be obtained/obtainable from RAFT or ATRP polymerisation processes. In one embodiment the polymer may be obtained/obtainable from a RAFT polymerisation process.

[0045] Methods of preparing polymers using ATRP, RAFT or nitroxide-mediated techniques are disclosed in the example section of US Patent Application US05/038146, examples 1 to 47.

[0046] More detailed descriptions of polymerisation mechanisms and related chemistry is discussed for nitroxide-mediated polymerisation (Chapter 10, pages 463 to 522), ATRP (Chapter 11, pages 523 to 628) and RAFT (Chapter 12, pages 629 to 690) in the Handbook of Radical Polymerization, edited by Krzysztof Matyjaszewski and Thomas P. Davis, 2002, published by John Wiley and Sons Inc (hereinafter referred to as "Matyjaszewski et al.").

[0047] The discussion of the polymer mechanism of ATRP polymerisation is shown on page 524 in reaction scheme 11.1, page 566 reaction scheme 11.4, reaction scheme 11,7 on page 571, reaction scheme 11.8 on page 572 and reaction scheme 11.9 on page 575 of Matyjaszewski et al.

[0048] In ATRP polymerisation, groups that may be transferred by a radical mechanism include halogens (from a halogen-containing compound) or various ligands. A more detailed review of groups that may be transferred is described in US 6,391,996, or paragraphs 61 to 65 of US Patent Application US05/038146.

[0049] Examples of a halogen-containing compound that may be used in ATRP polymerisation include benzyl halides such as p-chloromethylstyrene, α -dichloroxylene, α,α -dichloroxylene, α,α -dibromoxylene, hexakis(α -bromomethyl)benzene, benzyl chloride, benzyl bromide, 1-bromo-1-phenylethane and 1-chloro-1-phenylethane; carboxylic acid derivatives which are halogenated at the α -position, such as propyl 2-bromopropionate, methyl 2-chloropropionate, ethyl 2-chloropropionate, methyl 2-bromopropionate, and ethyl 2-bromoisobutyrate; tosyl halides such as p-toluenesulfonyl chloride; alkyl halides such as tetrachloromethane, tribromomethane, 1-vinylethyl chloride, and 1-vinylethyl bromide; and halogen derivatives of phosphoric acid esters, such as dimethylphosphoric acid.

[0050] In one embodiment when the halogen compound is employed, a transition metal such as copper is also present. The transition metal may be in the form of a salt. The transition metal is capable of forming a metal-to-ligand bond and the ratio of ligand to metal depends on the dentate number of the ligand and the co-ordination number of the metal. The ligand may be a nitrogen or phosphorus-containing ligand.

[0051] Examples of a suitable ligand include triphenylphosphine, 2,2-bipyridine, alkyl-2,2-bipyridine, such as 4,4-di-(5-heptyl)-2,2-bipyridine, tris(2-aminoethyl)amine (TREN), N,N,N',N',N''-pentamethyldiethylenetriamine, 4,4-di-(5-nonyl)-2,2-bipyridine, 1,1,4,7,10,10-hexamethyltriethylenetetramine and/or tetramethylethylenediamine. Further suitable ligands are described in, for example, International Patent application WO 97/47661. The ligands may be used individually or as a mixture. In one embodiment the nitrogen containing ligand is employed in the presence of copper. In one embodiment the ligand is phosphorus-containing with triphenyl phosphine (PPh₃) a common ligand. A suitable transition metal for a triphenyl phosphine ligand includes Rh, Ru, Fe, Re, Ni or Pd.

[0052] In RAFT polymerisation, chain transfer agents are important. A more detailed review of suitable chain transfer agents is found in paragraphs 66 to 71 of US Patent Application US05/038146. Examples of a suitable RAFT chain transfer agent include benzyl 1-(2-pyrrolidinone)carbodithioate, benzyl

(1,2-benzenedicarboximido) carbodithioate, 2-cyanoprop-2-yl 1-pyrrolicarbodithioate, 2-cyanobut-2-yl 1-pyrrolicarbodithioate, benzyl 1-imidazolecarbodithioate, N,N-dimethyl-S-(2-cyanoprop-2-yl)dithiocarbamate, N,N-diethyl-S-benzyl dithiocarbamate, cyanomethyl 1-(2-pyrrolidone) carbodithioate, cumyl dithiobenzoate, 2-dodecylsulphanylthiocarbonylsulphanyl-2-methyl-propionic acid butyl ester, O-phenyl-S-benzyl xanthate, N,N-diethyl S-(2-ethoxy-carbonylprop-2-yl)dithiocarbamate, dithiobenzoic acid, 4-chlorodithiobenzoic acid, O-ethyl-S-(1-phenylethyl)xanthate, O-ethyl-S-(2-(ethoxycarbonyl)prop-2-yl)xanthate, O-ethyl-S-(2-cyanoprop-2-yl)xanthate, O-ethyl-S-(2-cyanoprop-2-yl)xanthate, O-ethyl-S-cyanomethyl xanthate, O-pentafluorophenyl-S-benzyl xanthate, 3-benzylthio-5,5-dimethylcyclohex-2-ene-1-thione or benzyl 3,3-di(benzylthio)prop-2-enedithioate, S,S'-bis-(α,α' -disubstituted- α'' -acetic acid)-trithiocarbonate, S,S'-bis-(α,α' -disubstituted- α'' -acetic acid)-trithiocarbonate or S-alkyl-S'-(α,α' -disubstituted- α'' -acetic acid)-trithiocarbonates, benzyl dithiobenzoate, 1-phenylethyl dithiobenzoate, 2-phenylprop-2-yl dithiobenzoate, 1-acetoxyethyl dithiobenzoate, hexakis(thiobenzoylthiomethyl)benzene, 4-bis(thiobenzoylthiomethyl)benzene, 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene, 1,4-bis-(2-(thiobenzoylthio)-prop-2-yl)benzene, 1-(4-methoxyphenyl)ethyl dithiobenzoate, benzyl dithioacetate, ethoxycarbonylmethyl dithioacetate, 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate, 2,4,4-trimethylpent-2-yl dithiobenzoate, 2-(4-chlorophenyl)prop-2-yl dithiobenzoate, 3-vinylbenzyl dithiobenzoate, 4-vinylbenzyl dithiobenzoate, S-benzyl diethoxyphosphinyldithioformate, tert-butyl trithioperbenzoate, 2-phenylprop-2-yl 4-chlorodithiobenzoate, 2-phenylprop-2-yl 1-dithionaphthalate, 4-cyanopentanoic acid dithiobenzoate, dibenzyl tetrathioterephthalate, dibenzyl trithiocarbonate, carboxymethyl dithiobenzoate or poly(ethylene oxide) with dithiobenzoate end group or mixtures thereof.

[0053] In one embodiment a suitable RAFT chain transfer agent includes 2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl-propionic acid butyl ester, cumyl dithiobenzoate or mixtures thereof.

[0054] A discussion of the polymer mechanism of RAFT polymerisation is shown on page 664 to 665 in section 12.4.4 of Matyjaszewski et al.

[0055] When the polymer is prepared from anionic polymerisation techniques, initiators include, for example, hydrocarbyllithium initiators such as alkylolithium compounds (e.g., methyl lithium, n-butyl lithium, sec-butyl lithium), cycloalkyllithium compounds (e.g., cyclohexyl lithium and aryl lithium compounds (e.g., phenyl lithium, l-methylstyryl lithium, p-tolyl lithium, naphyl lithium and 1,1-diphenyl-3-methylpentyl lithium. Also, useful initiators include naphthalene sodium, 1,4-disodio-1,1,4,4-tetraphenylbutane, diphenylmethyl potassium or diphenylmethylnsodium.

[0056] The polymerisation process may also be carried out in the absence of moisture and oxygen and in the presence of at least one inert solvent. In one embodiment anionic polymerisation is conducted in the absence of any impurity which is detrimental to an anionic catalyst system. The inert solvent includes a hydrocarbon, an aromatic solvent or ether. Suitable solvents include isobutane, pentane, cyclohexane, benzene, toluene, xylene, tetrahydrofuran, diglyme, tetraglyme, orthoterphenyl, biphenyl, decalin or tetralin.

[0057] The anionic polymerisation process may be carried out at a temperature of 0 °C to -78 °C.

[0058] A more detailed description of process to prepare the polymer derived from anionic processes is discussed in International Patent Application WO 96/23012, page 3, line 11 to page 5, line 8. Page 7, line 25 to page 10, line 15 of WO 96/23012 further describes methods of preparing polymers by anionic polymerisation techniques. A detailed description of anionic polymerisation process is given in Textbook of Polymer Science, edited by Fred W. Billmeyer Jr., Third Edition, 1984, Chapter 4, pages 88-90.

[0059] The polymer may comprise at least one of (a) a polymer derived from monomers comprising: (i) a vinyl aromatic monomer; and (ii) a carboxylic monomer (typically maleic anhydride, maleic acid, (meth)acrylic acid, itaconic anhydride or itaconic acid) or derivatives thereof; (b) a poly(meth)acrylate; (c) a functionalised polyolefin; (d) an ethylene vinyl acetate copolymer; (e) a fumarate copolymer; (f) a copolymer derived from (i) an α -olefin and (ii) a

carboxylic monomer (typically maleic anhydride, maleic acid, (meth)acrylic acid, itaconic anhydride or itaconic acid) or derivatives thereof; or (g) mixtures thereof. In one embodiment the polymer with pendant groups comprises a polymethacrylate or mixtures thereof.

[0060] When the polymer is a polymethacrylate, the polymer may be derived from a monomer composition comprising:

(a) about 50 wt % to about 100 wt % (or about 65 wt % to about 95 wt %) of an alkyl methacrylate, wherein the alkyl group of the methacrylate has about 10 to about 30, or about 10 to about 20, or about 12 to about 18, or about 12 to about 15 carbon atoms;

(b) 0 wt % to about 40 wt % (or about 5 wt % to about 30 wt %) of an alkyl methacrylate, wherein the alkyl group of the methacrylate has about 1 to about 9, or about 1 to about 4 carbon atoms (for example methyl, butyl, or 2-ethylhexyl); and

(c) 0 wt % to about 10 wt % (or 0 wt % to about 5 wt %) of a nitrogen-containing monomer.

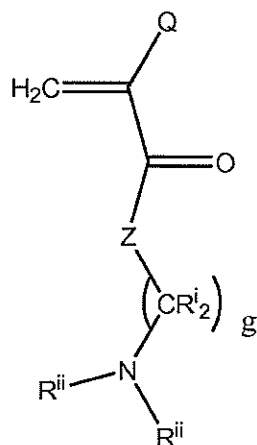
[0061] As used herein the term (meth)acrylate means acrylate or methacrylate units. The alkyl (meth)acrylate includes for example compounds derived from saturated alcohols, such as methyl methacrylate, butyl methacrylate, 2-methylpentyl, 2-propylheptyl, 2-butyloctyl, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl-(meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate; (meth)acrylates

derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 3-vinyl-2-butylcyclohexyl (meth)acrylate or bornyl (meth)acrylate.

[0062] The alkyl (meth)acrylates with long-chain alcohol-derived groups may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl methacrylate (by transesterification) with long-chain fatty alcohols, in which reaction a mixture of esters such as (meth)acrylate with alcohol groups of various chain lengths is generally obtained. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25 L of Shell AG; Lial® 125 of Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-11 and Acropol® 91 of Uguine Kuhlmann.

[0063] In one embodiment the star polymer is further functionalised in the core or the polymeric arms with a nitrogen-containing monomer. The nitrogen-containing monomer may include a vinyl-substituted nitrogen heterocyclic monomer, a dialkylaminoalkyl (meth)acrylate monomer, a dialkylaminoalkyl (meth)acrylamide monomer, a tertiary-(meth)acrylamide monomer or mixtures thereof.

[0064] In one embodiment the core or polymeric arms further comprise a (meth)acrylamide or a nitrogen containing (meth)acrylate monomer that may be represented by the formula:



wherein

Q is hydrogen or methyl and, in one embodiment, Q is methyl;

Z is an N-H group or O (oxygen);

each R^{ii} is independently hydrogen or a hydrocarbyl group containing about 1 to about 8, or about 1 to about 4 carbon atoms;

each R^i is independently hydrogen or a hydrocarbyl group containing 1 to 2 carbon atoms and, in one embodiment, each R^i is hydrogen; and

g is an integer in ranges including about 1 to about 6, or about 1 to about

3.

[0065] Examples of a suitable nitrogen-containing monomer include N,N-dimethylacrylamide, N-vinyl carbonamides such as N-vinyl-formamide, vinyl pyridine, N-vinylacetoamide, N-vinyl-n-propionamides, N-vinyl hydroxyacetoamide, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate (DMAEA), dimethylaminoethylmethacrylate (DMAEMA), dimethylaminobutylacrylamide, dimethylamine-propylmethacrylate (DMPMA), dimethylamine-propylacrylamide, dimethylaminopropylmethacrylamide, dimethylaminoethylacrylamide or mixtures thereof.

[0066] The polymer may be present at about 0.01 to about 12 wt %, or about 0,05 wt % to about 10 wt %, or about 0.075 to about 8 wt % of the lubricating composition.

Antiwear Agent

[0067] The antiwear agent is known. In one embodiment the antiwear agent comprises a phosphorus-containing acid, salt or ester, or mixtures thereof. In one embodiment the antiwear is in the form of a mixture.

[0068] The antiwear agent may be ash-containing (i.e. metal containing) or ashless (i.e. metal-free prior to being mixed with other components).

[0069] The antiwear agent may be derived phosphoric acid, phosphorous acid, thiophosphoric acid, thiophosphorous acid, or mixtures thereof.

[0070] The antiwear agent includes (i) a non-ionic phosphorus compound; (ii) an amine salt of a phosphorus compound; (iii) an ammonium salt of a phosphorus compound; (iv) a monovalent metal salt of a phosphorus

compound, such as a metal dialkyldithiophosphate or a metal dialkylphosphate; or (v) mixtures of (i), (ii), (iii) or (iv).

[0071] In one embodiment the antiwear agent comprises a metal dialkyldithiophosphate or a metal dialkylphosphate. The alkyl groups of the dialkyldithiophosphate and/or the dialkylphosphate may be linear or branched containing about 2 to about 20 carbon atoms, provided that the total number of carbons is sufficient to make the metal dialkyldithiophosphate oil soluble. The metal of the metal dialkyldithiophosphate and/or dialkylphosphate typically includes monovalent or divalent metals. Examples of suitable metals include sodium, potassium, copper, calcium, magnesium, barium or zinc. In one embodiment the antiwear agent comprises a zinc dialkyldithiophosphate or mixtures thereof. In one embodiment the antiwear agent comprises a zinc dialkylphosphate or mixtures thereof.

[0072] Examples of a suitable zinc dialkylphosphate often referred to as ZDDP, ZDP or ZDTP). include zinc di-(2-methylpropyl) dithiophosphate, zinc di-(amyl) dithiophosphate, zinc di-(1,3-dimethylbutyl) dithiophosphate, zinc di-(heptyl) dithiophosphate, zinc di-(octyl) dithiophosphate di-(2-ethylhexyl) dithiophosphate, zinc di-(nonyl) dithiophosphate, zinc di-(decyl) dithiophosphate, zinc di-(dodecyl) dithiophosphate, zinc di-(dodecylphenyl) dithiophosphate, zinc di-(heptylphenyl) dithiophosphate, or mixtures thereof.

[0073] In one embodiment the antiwear agent is other than metal dialkyldithiophosphate.

[0074] In one embodiment the antiwear agent comprises an ammonium or amine salt of a phosphorus-containing acid or ester.

[0075] The amine salt of a phosphorus acid or ester includes phosphoric acid esters and amine salts thereof; dialkyldithiophosphoric acid esters and amine salts thereof; amine salts of phosphites; and amine salts of phosphorus-containing carboxylic esters, ethers, and amides; and mixtures thereof.

[0076] The amine salt of a phosphorus acid or ester may be used alone or in combination. In one embodiment the amine salt of a phosphorus compound is derived from an amine salt of a phosphorus compound, or mixtures thereof.

[0077] In one embodiment the amine salt of a phosphorus acid or ester includes a partial amine salt-partial metal salt compounds or mixtures thereof. In one embodiment the amine salt of a phosphorus acid or ester further comprises a sulphur atom in the molecule.

[0078] The amines which may be suitable for use as the amine salt include primary amines, secondary amines, tertiary amines, and mixtures thereof. The amines include those with at least one hydrocarbyl group, or, in certain embodiments, two or three hydrocarbyl groups. The hydrocarbyl groups may contain about 2 to about 30 carbon atoms, or in other embodiments about 8 to about 26, or about 10 to about 20, or about 13 to about 19 carbon atoms.

[0079] Primary amines include ethylamine, propylamine, butylamine, 2-ethylhexylamine, octylamine, and dodecylamine, as well as such fatty amines as n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine and oleyamine. Other useful fatty amines include commercially available fatty amines such as "Armeen®" amines (products available from Akzo Chemicals, Chicago, Illinois), such as Armeen C, Armeen O, Armeen OL, Armeen T, Armeen HT, Armeen S and Armeen SD, wherein the letter designation relates to the fatty group, such as coco, oleyl, tallow, or stearyl groups.

[0080] Examples of suitable secondary amines include dimethylamine, diethylamine, dipropylamine, dibutylamine, diamylamine, dihexylamine, diheptylamine, methylethylamine, ethylbutylamine and ethylamylamine. The secondary amines may be cyclic amines such as piperidine, piperazine and morpholine.

[0081] The amine may also be a tertiary-aliphatic primary amine. The aliphatic group in this case may be an alkyl group containing about 2 to about 30, or about 6 to about 26, or about 8 to about 24 carbon atoms. Tertiary alkyl amines include monoamines such as tert-butylamine, tert-hexylamine, 1-methyl-1-amino-cyclohexane, tert-octylamine, tert-decylamine, tertdodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetracosanylamine, and tert-octacosanylamine.

[0082] In one embodiment the amine salt of a phosphorus acid or ester includes an amine with C11 to C14 tertiary alkyl primary groups or mixtures thereof. In one embodiment the amine salt of a phosphorus compound includes an amine with C14 to C18 tertiary alkyl primary amines or mixtures thereof. In one embodiment the amine salt of a phosphorus compound includes an amine with C18 to C22 tertiary alkyl primary amines or mixtures thereof.

[0083] Mixtures of amines may also be used in the invention. In one embodiment a useful mixture of amines is "Primene® 81R" and "Primene® JMT." Primene® 81R and Primene® JMT (both produced and sold by Rohm & Haas) are mixtures of C11 to C14 tertiary alkyl primary amines and C18 to C22 tertiary alkyl primary amines respectively.

[0084] In one embodiment the amine salt of a phosphorus acid or ester is the reaction product of a C14 to C18 alkylated phosphoric acid with Primene 81R™ (produced and sold by Rohm & Haas) which is a mixture of C11 to C14 tertiary alkyl primary amines.

[0085] Examples of the amine salt of a phosphorus acid or ester include the reaction product(s) of isopropyl, methyl-amyl (1,3-dimethylbutyl or mixtures thereof), 2-ethylhexyl, heptyl, octyl, nonyl, decyl, dodecyl, butadecyl, hexadecyl, octadecyl or eicosyl phosphoric (or dithiophosphoric) acids with ethylene diamine, morpholine, 2-ethylhexyl amine or Primene 81R™, and mixtures thereof. In one embodiment the antiwear agent comprises an amine salt of a phosphorus acid or ester or mixtures thereof. In one embodiment the phosphorus acid or ester is a C14-C18-alkyl phosphorus acid or ester with Primene 81R™ or 2-ethylhexyl amine.

[0086] In one embodiment a dithiophosphoric acid may be reacted with an epoxide or a glycol. This reaction product is further reacted with a phosphorus acid, anhydride, or lower ester. The epoxide includes an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, styrene oxide and the like. In one embodiment the epoxide is propylene oxide. The glycols may be aliphatic glycols having about 1 to about 12, or about 2 to about 6, or about 2 to about 3 carbon atoms. The dithiophosphoric acids, glycols, epoxides, inorganic

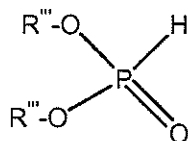
phosphorus reagents and methods of reacting the same, are described in U.S. Patent numbers 3,197,405 and 3,544,465. The resulting acids may then be salted with amines. An example of suitable dithiophosphoric acid is prepared by adding phosphorus pentoxide (about 64 grams) at about 58 °C over a period of about 45 minutes to about 514 grams of hydroxypropyl O,O-di(1,3-dimethylbutyl)phosphorodithioate (prepared by reacting di(1,3-dimethylbutyl)-phosphorodithioic acid with about 1.3 moles of propylene oxide at about 25 °C). The mixture is heated at about 75 °C for about 2.5 hours, mixed with a diatomaceous earth and filtered at about 70 °C. The filtrate contains about 11.8% by weight phosphorus, about 15.2% by weight sulphur, and an acid number of about 87 (bromophenol blue).

[0087] In one embodiment the antiwear agent comprises an amide-containing dithiophosphorus acid ester. A more detailed description for the amide-containing dithiophosphorus acid ester is found in US 4,938,884. A description of the molecular structure is found in column 2, lines 4 to 28. Suitable examples prepared are disclosed in Examples 1 to 7 (column 8, line 45 to column 10, line 13 of US 4,938,884). Typically the amide-containing dithiophosphorus acid ester is prepared by the addition of dithiophosphoric acid to an acrylate, such as, methyl acrylate.

[0088] In one embodiment the antiwear agent comprises a carboxylic-containing dithiophosphorus acid ester, for example 3-(bis-pentoxothiophosphorylsulphanyl)-propionic acid methyl ester, 3-(dibutoxythiophosphorylsulphanyl)-propionic acid methyl ester, or mixtures thereof.

[0089] In one embodiment the antiwear agent comprises a non-ionic phosphorus compound. Typically the non-ionic phosphorus compound may have an oxidation of +3 or +5. The different embodiments comprise phosphite ester, phosphate esters, or mixtures thereof.

[0090] In one embodiment the antiwear agent comprises a non-ionic phosphorus compound that is a hydrocarbyl phosphite. The hydrocarbyl-substituted phosphite of the invention includes those represented by the formula:



wherein each R''' may be independently hydrogen or a hydrocarbyl group, with the proviso that at least one of the R''' groups is hydrocarbyl.

[0091] Each hydrocarbyl group of R''' may contain at least about 2 or about 4 carbon atoms. Typically, the combined total sum of carbon atoms present on both R''' groups may be less than about 45, less than about 35 or less than about 25. Examples of suitable ranges for the number of carbon atoms present on both R''' groups includes about 2 to about 40, about 3 to about 24, or about 4 to about 20. Examples of suitable hydrocarbyl groups include propyl, butyl, t-butyl, pentyl, hexyl dodecyl, butadecyl, hexadecyl, or octadecyl groups. Generally the hydrocarbyl phosphite is soluble or at least dispersible in oil. In one embodiment the hydrocarbyl phosphite may be di-butyl hydrogen phosphite or a C₁₆₋₁₈ alkyl hydrogen phosphite. A more detailed description of the non-ionic phosphorus compound include column 9, line 48 to column 11, line 8 of US 6,103,673.

[0092] In one embodiment the antiwear agent comprises a phosphate ester. Examples of a suitable phosphate ester include triaryl phosphates such as tricresyl phosphate, triphenyl phosphate, tri-dimethylphenyl phosphate, tri-butylphenyl phosphate, or mixtures thereof.

[0093] In one embodiment the antiwear agent comprises a thiophosphate ester. Examples of a suitable thiophosphate ester include triaryl thiophosphates such as tricresyl thiophosphate, triphenyl thiophosphate, tri-dimethylphenyl thiophosphate, tri-butylphenyl thiophosphate, or mixtures thereof.

[0094] The antiwear agent may be present at about 0.0001 wt % to about 5 wt %, or about 0.001 wt % to about 2 wt %, or about 0.05 wt % to about 1.5 wt %, or about 0.1 wt % to about 1 wt % of the lubricating composition.

Corrosion Inhibitor

[0095] The corrosion inhibitor of the invention may also be described as metal deactivators or a yellow-metal passivator.

[0096] Examples of a corrosion inhibitor comprises at least one of benzotriazoles, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N-dialkyldithiocarbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercapto thiadiazoles or mixtures thereof. In one embodiment the corrosion inhibitor is benzotriazole. In one embodiment the corrosion inhibitor is a 2,5-bis(alkyl-dithio)-1,3,4-thiadiazole. The corrosion inhibitor may be used alone or in combination with other corrosion inhibitors.

[0097] Benzotriazoles may contain hydrocarbyl substitutions on at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7-. The hydrocarbyl groups may contain 1 to about 30, or 1 to about 15, or 1 to about 7 carbon atoms. In one embodiment the corrosion inhibitor is tolyltriazole. In one embodiment hydrocarbyl benzotriazoles substituted at positions 4- or 5- or 6- or 7- can be further reacted with an aldehyde and a secondary amine.

[0098] Examples of suitable hydrocarbyl benzotriazoles further reacted with an aldehyde and a secondary amine include N,N-bis(heptyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(nonyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(decyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(undecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(dodecyl)-ar-methyl-1H-benzotriazole-1-methanamine, N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine and mixtures thereof. In one embodiment the corrosion inhibitor is N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine.

[0099] In one embodiment, the corrosion inhibitor is 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles. The alkyl groups of 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles contains 1 to about 30, or about 2 to about 25, or 4 to about 20, or about 6 to about 16 carbon atoms. Examples of suitable 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles include 2,5-bis(tert-octyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-decyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-undecyldithio)-1,3,4-thiadiazole, 2,5-bis(tert-dodecyldithio)-1,3,4-thiadiazole, or mixtures thereof.

[00100] The corrosion inhibitor may be present at about 0.0001 wt % to about 5 wt %, or about 0.0001 wt % to about 0.5 wt %, or about 0.0001 wt % to about 0.1 wt %, or about 0.0005 wt % to about 0.05 wt % of the lubricating composition.

Oils of Lubricating Viscosity

[00101] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[00102] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[00103] Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[00104] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[00105] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil, lard oil), mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types and oils derived from coal or shale or mixtures thereof.

[00106] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls);

alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[00107] Other synthetic lubricating oils include polyol esters (such as Prolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[00108] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index 80-120); Group III (sulphur content ≤ 0.03 wt %, and ≥ 90 wt % saturates, viscosity index ≥ 120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil or mixtures thereof. Alternatively the oil of lubricating viscosity is often an API Group II, Group III or Group IV oil or mixtures thereof.

[00109] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the polymer, the antiwear agent, the corrosion inhibitor and other performance additives.

[00110] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the polymer, the antiwear agent and the corrosion inhibitor are in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components (a), (b) and (c) (i.e. the polymer, the antiwear agent; and the

corrosion inhibitor to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

Other Performance Additive

[00111] The composition of the invention optionally further includes at least one other performance additive. The other performance additives include dispersants, detergents, viscosity index improvers (that is, viscosity modifiers other than the polymer (i.e. component (a) of the invention), antioxidants, foam inhibitors, demulsifiers, pour point depressants, foam inhibitors, a carboxylic acid or anhydride, and mixtures thereof.

[00112] The total combined amount of the other performance additive compounds present on an oil free basis may include ranges of 0 wt % to about 25 wt %, or about 0 wt % to about 10 wt %, or about 0.005 wt % to about 5 wt %, or about 0.005 wt % to about 1 wt %, or about 0.005 wt % to about 0.5 wt % of the composition. Although one or more of the other performance additives may be present, it is common for the other performance additives to be present in different amounts relative to each other.

[00113] A suitable dispersant may be a succinimide dispersant (for example N-substituted long chain alkenyl succinimides), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant, a polyetheramine dispersant. In different embodiments the dispersant may be a succinimide, succinic acid ester, or Mannich dispersant.

[00114] In one embodiment the succinimide dispersant comprises a polyisobutylene succinimide, wherein the polyisobutylene has a number average molecular weight of about 400 to about 5000.

[00115] Succinimide dispersants and their methods of preparation are more fully described in U.S. Patents 4,234,435 and 3,172,892.

[00116] Hydrocarbyl-amine dispersants are hydrocarbyl-substituted amines. The hydrocarbyl-substituted amine may be formed by heating a mixture of a chlorinated olefin or polyolefin such as a chlorinated polyisobutylene with an

amine such as ethylenediamine in the presence of a base such as sodium carbonate as described in U.S. Patent No. 5,407,453.

[00117] In one embodiment the invention further comprises at least one dispersant derived from polyisobutylene, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc may be used alone or in combination. In one embodiment the dispersant comprises a polyisobutylene succinimide complex with zinc or mixtures thereof and described in more detail in US 3,163,603.

[00118] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, phosphorus compounds and/or metal compounds. In one embodiment the dispersant is a borated dispersant. Typically the borated dispersant comprises the succinimide dispersant comprises a polyisobutylene succinimide, wherein the polyisobutylene has a number average molecular weight of 140 to 5000.

[00119] The dispersant may be present at 0 wt % to about 5 wt %, or about 0.05 to about 2.5 wt %, or about 0.1 to about 1.5 wt % of the lubricating composition.

[00120] Antioxidants include molybdenum compounds such as molybdenum dithiocarbamates, sulphurised olefins, sulphides such as tert-nonyl mercaptan reacted with propylene oxide (mole ratio 1:1), hindered phenols (2,6-di-tert-butyl-4-methylphenol, 2,6-di-t-butylphenol, 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid butyl ester, 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid isooctyl ester or 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid 2-ethylhexyl ester), aminic compounds such as phenylaphanaphthylamine or alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine, butyl octyl diphenylamine, octyl styrenyl diphenylamine or diethyl dinonyl diphenylamine).

[00121] The antioxidant may be present at 0 to about 3 wt %, or about 0.01 to about 1.5 wt %, or about 0.05 to about 0.8 wt % or the lubricating composition.

[00122] The detergent may be natural or synthetic. In one embodiment the detergent is synthetic.

[00123] The detergent may be a phenate or a sulphurised-phenate, a sulphonate, an alkyl salicylate, a salixarate, a saligenin, or mixtures thereof.

[00124] In one embodiment the detergent comprises a phenate or a sulphurised-phenate.

[00125] In one embodiment the detergent comprises a sulphonate detergent. The sulphonate detergent may also have corrosion inhibitor properties.

[00126] The sulphonate detergent of the composition includes compounds represented by the formula: $(R^1)_k-A-SO_3M$, wherein each R^1 is a hydrocarbyl group in one embodiment containing about 6 to about 40, or about 8 to about 35, or about 8 to about 30, or about 8 to about 20 carbon atoms; A may be independently a cyclic or acyclic divalent or multivalent hydrocarbon group; M is hydrogen, a valence of a metal ion, an ammonium ion or mixtures thereof; and k is an integer of 0 to about 5, for example 0, 1, 2, 3, 4, 5. In one embodiment k is 1, 2 or 3, in another embodiment 1 or 2 and in another embodiment 2.

[00127] In one embodiment k is 1 and R^1 is a branched alkyl group with about 6 to about 40 carbon atoms. In one embodiment k is 1 and R^1 is a linear alkyl group with about 6 to about 40 carbon atoms.

[00128] Examples of suitable R^1 linear alkyl group include octyl, nonyl, decyl, undecyl, dodecyl, pentadecyl, hexadecyl, eicosyl, or mixtures thereof.

[00129] When M is a valence of a metal ion, the metal may be monovalent, divalent, trivalent or mixtures of such metals. When monovalent, the metal M includes an alkali metal such as lithium, sodium, or potassium, and when divalent, the metal M includes an alkaline earth metal such as magnesium, calcium or barium. In one embodiment the metal is an alkaline earth metal. In one embodiment the metal is calcium.

[00130] When A is cyclic hydrocarbon group, suitable groups include phenylene or fused bicyclic groups such as naphthylene, indenylene,

indanylene, bicyclopentadienylylene or mixtures thereof. In one embodiment A comprises a naphthylene ring.

[00131] In different embodiments the detergent is neutral or overbased. In one embodiment the detergent is neutral.

[00132] Examples of a suitable detergent include at least one of calcium C₈-₂₀-alkyl substituted benzene sulphonate, calcium dinonyl naphthalene sulphonate, calcium didecyl naphthalene sulphonate, didodecyl naphthalene sulphonate, calcium dipentadecyl naphthalene sulphonate, or mixtures thereof. In one embodiment the detergent comprises neutral or slightly overbased calcium dinonyl naphthalene sulphonate, or mixtures thereof.

[00133] The detergent may be present in the lubricating composition in ranges from 0 to about 3 wt %, or about 0.001 to about 1.5 wt %, or about 0.01 to about 0.75 wt %.

[00134] Viscosity modifiers other than the polymer (a) of the invention, including hydrogenated copolymers of styrene-butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylate, polyacrylate, polyalkyl styrenes, alkenyl aryl conjugated diene copolymers, polyolefins, and esters of maleic anhydride-styrene copolymers. Conventional poly(meth)acrylate polymers may be derived from monomers substantially the same as those defined for the polymeric arms. However, the conventional poly(meth)acrylate is generally free of a functional group selected from a halogen, an -O-N= group and a -S-C(=S)- group. In one embodiment the polymer of the invention is mixed with a conventional viscosity modifier.

[00135] The viscosity modifier other than polymer (a) of the invention may be present at 0 wt % to about 15 wt %, or about 0.01 to about 12 wt %, or about 0.05 to about 10 wt %, or about 0.075 to about 8 wt % of the lubricating composition.

[00136] The carboxylic acid or anhydride thereof may contain about 10 to about 400, or about 20 to about 200, or about 30 to about 150 carbon atoms.

[00137] The carboxylic acid or anhydride thereof may be derived from a polyolefin. The polyolefin may be a homopolymer, copolymer, or

interpolymer. The polyolefin may be prepared from polymerisable monomers containing about 2 to about 16, or about 2 to about 8, or about 2 to about 6 carbon atoms. Often the polymerisable monomers comprise one or more of propylene, isobutene, 1-butene, isoprene, 1,3-butadiene, or mixtures thereof.

[00138] In one embodiment the carboxylic acid or anhydride thereof, or derivatives thereof comprises a succinic acid, anhydride thereof, or carboxylic ester thereof.

[00139] In one embodiment the carboxylic acid or anhydride thereof comprises a polyisobutylene succinic acid or anhydride thereof. A more detailed description of a suitable carboxylic acid or anhydride thereof is described in WO 93/03121, page 33, line 10 to page 37, line 20.

[00140] In one embodiment the carboxylic acid or anhydride thereof, or derivatives thereof comprises the reaction product of dodecenyl succinic acid with propylene oxide.

[00141] The carboxylic acid or anhydride thereof may be present in ranges from 0 to about 3 wt %, or from about 0.0001 to about 3 wt %, or from about 0.001 to about 1 wt %, or from about 0.01 to about 0.5 wt % of the lubricating composition.

[00142] Other performance additives such as foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides; and seal swell agents including Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil (FN 3200); and dispersant viscosity modifiers (often referred to as DVM) include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or styrene-maleic anhydride copolymers reacted with an amine; may also be used in the composition of the invention.

Industrial Application

[00143] The method of the invention is useful for lubricating a variety of mechanical devices. The mechanical device comprises at least one of an internal combustion engine (for crankcase lubrication), a hydraulic system, a turbine system, a circulating oil system, an industrial oil system, a gear, a gearbox, an automatic transmission or a manual transmission.

[00144] In different embodiments the mechanical device comprises at least one of a hydraulic system, a turbine system, a circulating oil system, or an industrial oil system.

[00145] The following examples provide illustrations of the invention. These examples are non exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[00146] Preparative Example 1 (Prep 1) is prepared in a vessel equipped with a nitrogen inlet flowing at about 28.3 L/hr, medium speed mechanical stirrer, a thermocouple and a water-cooled condenser is charged with about 80 g of C₁₂₋₁₅ alkyl methacrylate, about 20g of Methyl methacrylate, about 0.55 g of TrigonoxTM-21 (initiator), about 4.07 g of 2-dodecylsulphanylthiocarbonylsulphanyl-2-methylpropionic acid dodecyl ester (chain transfer agent) and about 48.2 g of oil. The contents of the vessel are stirred under a nitrogen blanket for about 20 minutes to ensure sufficient mixing. The nitrogen flow is reduced to about 14.2 L/hr and the mixture is set to be heated to about 90 °C for about 3 hours. About 6.05 g of ethylene glycol dimethacrylate is added to the vessel and the mixture is stirred at about 90 °C for an additional about 3 hours. The resultant product is a mixture of polymers and is then cooled to ambient temperature. The major product fraction is characterised as having a weight average molecular weight of about 283,300 g/mol and having a number average molecular weight of about 215,900 g/mol. The polymer is believed to have at least 9 polymeric arms (containing about 80 wt % of C₁₂₋₁₅ alkylmethacrylate, about 20 wt % of methyl methacrylate) and the conversion to a star polymer is 72 %, with 28 % uncoupled linear polymer chains.

[00147] Comparative Example 1 (CE1) is a linear polymethacrylate prepared in a equipped with a nitrogen inlet flowing at about 28.3 L/hr, medium speed

mechanical stirrer, a thermocouple and a water-cooled condenser is charged with about 381.4 g of C₁₂₋₁₅ alkylmethacrylate, about 62.28 g of methyl methacrylate, about 110.9 g of oil, about 3.12 g of Trigonox™ 21 initiator and 3.12 g of n-dodecyl mercaptan. The contents of the vessel are shaken and mixed to ensure sufficient mixing. About one-third of the vessel contents are transferred into another vessel containing equipped with a mechanical overhead stirrer, water-cooled condenser, thermocouple, addition funnel and nitrogen inlet. The contents of the vessel are stirred for about 30 minutes under a nitrogen blanket (flow rate of about 28.3 L/hr. The vessel is then heated to about 110 °C with a nitrogen flow rate of about 14.2 L/hr. After the reaction temperature reaches an exotherm peak, the remaining two-thirds of the 2/3 of monomer mixture (from the first vessel) is added through the addition funnel over a period of about 90 minutes, before cooling the vessel to about 110 °C until the end of reaction. The vessel is charged with about 0.2 g of Trigonox™ 21 in about 1.8 g of oil and stirred for about one hour. This step is repeated 3 more times. The contents of the vessel are stirred for about one hour before cooling to ambient temperature. The resultant polymer is characterised as having a weight average molecular weight of 36,600 g/mol and number average molecular weight of 19,900 g/mol.

[00148] Hydraulic system lubricating compositions are prepared containing the polymers of Prep1 or CE1, other additives and base oil. Lubricating composition 1 (LC1) contains about 6.18 wt % of Prep1 and further contains a total of about 0.85 wt % of all other additives (i.e. a zinc containing antiwear agent, a benzotriazole corrosion inhibitor, a naphthalene sulphonate, an antioxidant, a phenate detergent, an antifoam agent, a dispersant and about 0.2 wt % of a polyacrylate pour point depressant). A reference lubricating composition (RLC1) is the same as LC1; except the polymer of CE1 is used at about 8.2 wt % and the base oil is reduced accordingly.

[00149] The lubricating compositions are evaluated by determining the kinematic viscosities at about 100°C and at about 40°C (by employing ASTM method D445). The viscosity index (VI) is also determined by employing ASTM method D2270. The results obtained are as follows:

Test	LC1	RLC1
Kinematic Viscosity at 100 °C (mm ² /s)	8.2	8.0
Kinematic Viscosity at 40 °C (mm ² /s)	47.3	45.1
Viscosity Index	149	153

[00150] The lubricating composition is also subjected to shear as determined by KRL tapered bearing shear stability test. The instrument is run for about 20 hours with about 5000 N load, at about 140 °C and at about 1450 rpm. The viscosity data obtained from the test is described in ASTM method D445. The results obtained are:

Test	LC1	RLC1
New Oil Kinematic Viscosity at 100 °C (mm ² /s)	8.32	8.062
After Test Kinematic Viscosity at 100 °C (mm ² /s)	7.26	6.857
Shear Loss (%)	12.74	14.95

[00151] The lubricating compositions are subjected to evaluation using ASTM Method D4310. The test evaluates the tendency of inhibited mineral oil based steam turbine lubricants and antiwear hydraulic lubricants to corrode copper catalyst metal and to form sludge during operation in the presence of water, oxygen, and copper and iron metals at an elevated temperature. The test duration is about 1000 hours at about 95 °C. The results obtained are as follows:

D4310 Test Parameter Measured	Test Pass Limits	LC1	RLC1
Sludge Accumulation	100 mg (max)	82.6	80.8
Copper in Oil		144.7	140.4
Copper in Water		3	15.1
Copper in Sludge		10.8	27.45
Total Amount Copper	200 mg (max)	158.5	182.95
Copper Rating		1B	4A
Steel Rating		Bright	Tarnished

[00152] The data obtained indicate that the lubricating compositions of the invention provide improved Kinematic viscosity control at a lower treat rate than a comparative example whilst maintaining the appropriate lubricating performance for a hydraulic system.

[00153] While the invention has been explained in relation to its various embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A lubricating composition comprising:
 - (a) 0.001 to 15 wt % of a polymethacrylate polymer with (i) a weight average molecular weight of 120,000 to 700,000; and (ii) a shear stability index of 30 to 60, wherein the polymer has radial or star architecture, and wherein the polymethacrylate is derived from a monomer composition consisting essentially of:
 - (a) 50 wt % to 100 wt % of an alkyl methacrylate, wherein the alkyl group of the methacrylate has 12 to 15 carbon atoms;
 - (b) 0 wt % to 40 wt % of an alkyl methacrylate, wherein the alkyl group of the methacrylate has 1 to 9 carbon atoms; and
 - (c) 0 wt % to 10 wt % of a nitrogen containing monomer;
 - (b) an antiwear agent;
 - (c) a corrosion inhibitor; and
 - (d) an oil of lubricating viscosity.
2. The lubricating composition of claim 1, wherein the shear stability index is 20 to 90, or 30 to 60.
3. The lubricating composition of claim 1 or 2, wherein the lubricating composition further comprises a component of linear polymer chains.
4. The lubricating composition of any one of claims 1 to 3, wherein the polymer has a random, tapered, di-block, tri-block, or multi-block architecture.
5. The lubricating composition of any one of claims 1 to 4, wherein the polymer is derived from 20 wt % or more of a mono-vinyl monomer.
6. The lubricating composition of any one of claims 1 to 5, wherein the polymer is obtained from RAFT or ATRP polymerisation processes.
7. The lubricating composition of claim 6, wherein the polymer is obtained from RAFT polymerisation processes.
8. The lubricating composition of any one of claims 1 to 7, wherein the polymer is present at 0.01 to 12 wt %, or 0.075 to 8 wt % of the lubricating composition.
9. The lubricating composition of any one of claims 1 to 8, wherein the antiwear agent comprises at least one of (i) a non-ionic phosphorus compound; (ii) an amine salt of a phosphorus compound; (iii) ammonium salt of a phosphorus compound; (iv) a monovalent metal salt of a phosphorus compound; or (v) mixtures of (i), (ii), (iii) or (iv).

10. The lubricating composition of any one of claims 1 to 9, wherein the antiwear agent comprises a metal dialkyldithiophosphate or a metal dialkylphosphate.

11. The lubricating composition of any one of claims 1 to 10, wherein the antiwear agent is present at 0.0001 wt % to 5 wt %, or 0.1 wt % to 1 wt % of the lubricating composition.

12. The lubricating composition of any one of claims 1 to 11, wherein the corrosion inhibitor comprises at least one of a benzotriazoles, or a 2,5-bis(alkyl-dithio)-1,3,4-thiadiazole.

13. The lubricating composition of any one of claims 1 to 12, wherein the corrosion inhibitor is present at 0.0001 wt % to 5 wt %, or 0.0005 wt % to 0.05 wt % of the lubricating composition.

14. The lubricating composition of any one of claims 1 to 13 further comprises a detergent, wherein the detergent comprises at least one of a phenate, a sulphurised phenate or a sulphonate.

15. The lubricating composition of claim 14, wherein the sulphonate contains a naphthalene ring.

16. The lubricating composition of claim 14, wherein the sulphonate comprises at least one of at least one of calcium dinonyl naphthalene sulphonate, calcium didecyl naphthalene sulphonate, didodecyl naphthalene sulphonate, calcium dipentadecyl naphthalene sulphonate, or mixtures thereof.

17. The lubricating composition of claims 14, 15 or 16 wherein the sulphonate is present at 0 to 3 wt%, 0.001 to 1.5 wt %, or 0.01 to 0.75 wt %.

18. The lubricating composition of any one of claims 1 to 17, wherein the lubricating composition comprises:

- (a) 0.001 to 15 wt % of the polymethacrylate polymer;
- (b) 0.0001 wt % to 5 wt % of an antiwear agent;
- (c) 0.0001 wt % to 5 wt % of a corrosion inhibitor;
- (d) 0 wt % to 3 wt % of a detergent; and
- (e) 87 wt % to 99.98 wt % of an oil of lubricating viscosity.

19. A method for lubricating a mechanical device comprising a supplying to the mechanical device a lubricating composition, wherein the mechanical device is a hydraulic system, and wherein the lubricating composition comprises the lubricating composition of any one of claims 1 to 18.